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EUROPEAN PATENT APPLICATION

(21) Application number: 8530/506.7

(51) Int. Cl.⁴: C 08 F 8/30

(22) Date of filing: 17.10.85

(30) Priority: 18.10.84 US 662064

(43) Date of publication of application:
23.04.86 Bulletin 86/17

(64) Designated Contracting States:
DE FR GB IT NL

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(64) Heat stable tetrafluoroethylene-perfluoro (alkyl vinyl ether) copolymers.

(57) A tetrafluoroethylene-perfluoro(alkyl vinyl ether copoly-
me) in which heat unstable carbinol end-groups ($-\text{CH}_2\text{OH}$
groups) present have been protected against heat degrada-
tion by treating the copolymer with NH_3 or NH_3 producing
compounds.

-COOH, groups with evolution of hydrogen fluoride (HF). HF is a reactive, corrosive acid and its presence causes difficulties in molded articles derived from TFE/FAVE copolymers that contain the original -CH₂OH end groups. In addition, the -COOH groups degrade on fabrication of the polymer to produce gases (CO₂) that produce undesirable bubbles in molded articles.

The raw polymer, as made, contains some -COF and -COOH end-groups and these decompose also, along with the -COF and -COOH groups formed from decomposition of the -CH₂OH end-groups.

SUMMARY OF THE INVENTION

In an effort to reduce the number of -COF and -COOH end-groups, it has now been discovered that those groups present in the raw polymer, as made, can be converted to amide end-groups. It has also now been discovered that this conversion to amide groups of the original -COF and -COOH end-groups surprisingly imparts thermal stability to the -CH₂OH end-groups and retards their decomposition. Accordingly, this invention is directed to a means for stabilizing the carbinol (-CH₂OH) end groups to retard their decomposition to -COF groups and, in turn, the breakdown of the -COF groups to form corrosive HF and undesirable -COOH end groups. The stabilizing means is not completely known or understood, but it has now been found that when TFE/FAVE copolymers containing -CH₂OH, -COF and -COOH end groups (which are conveniently made in the presence of halocarbon solvents and an alcohol) are treated with nitrogen-containing compounds such as ammonia or ammonia-producing compounds such as ammonium salts or organic amines, the resulting material has enhanced propensity against

To treat these copolymers with nitrogen compounds to convert the -COF and -COOH groups to amide groups, the copolymer is simply contacted with the nitrogen compound. Ammonia vapor is the preferred nitrogen compound and it can be simply passed into a closed container containing the copolymer for a desired amount of time or can be passed over or through a bed of the copolymer for a desired amount of time. The copolymer can be agitated during contact if desired. The form of the copolymer is not important; it can be in flake, cube, pellet or article form. The atmosphere in the container can be 100% NH_3 or can be as little as 0.1% by volume NH_3 (with the remainder being air or inert gases). In dilute form, 1-30% by volume is preferred and 10-30% most preferred. Contact time is long enough to achieve the desired degree of conversion to amide end groups, usually at least 50%, and preferably about 100%. The time is usually between 1/2 to 24 hours, with 1 to 7 1/2 hours preferred and 2 to 6 hours most preferred. Temperature and pressure are not critical. Pressure is usually atmospheric, for convenience. Temperature is usually room temperature, 20-30°C, but can be between 0 and 100°C. Usually when -COOH groups are to be converted to amide groups, higher temperatures are used.

When ammonia-forming ammonium salts or organic amines are used, the copolymer is ordinarily melted in contact with the nitrogen compound. A convenient means is to extrude the molten copolymer and the nitrogen compound. Among the nitrogen compounds that can be employed in this manner are

copolymer in water and measuring the amount of fluoride ions extracted into the water. Typically, raw copolymer will liberate 20ppm or more F^- ions based on weight of copolymer, whereas the treated
 5 copolymer liberates less than 5ppm F^- , and preferably less than 1.

DESCRIPTION OF MATERIALS AND TEST MEASUREMENTS

A. Polymer End Groups

The type and quantity of certain end groups
 10 in the polymer were determined by the infrared spectrum obtained on compression molded films of about 10 mils (0.25 mm) thickness. The end groups of interest and absorbance frequencies are shown below:

	<u>End Group</u>	<u>Absorbance</u>
15	Acid Fluoride (-COF)	1883 cm^{-1}
	Carboxylic Acid (m) (-CO ₂ H)	1810 cm^{-1}
	Methyl Ester (-CO ₂ CH ₃)	1795 cm^{-1}
20	Carboxamide (-CONH ₂)	1768 cm^{-1}
	Carbinol (-CH ₂ OH)	3648 cm^{-1}

The quantitative measurement of the number of these groups was obtained by the measurement of
 25 the extinction coefficients of each of these groups from model compounds and transferring these coefficients to the measurements obtained on the polymer. The end groups are expressed as the number per one million carbon atoms in the polymer.

30 B. Melt Viscosity

The melt viscosity is measured according to ASTM D-1238-52T modified by using a cylinder, orifice and piston tip made of a corrosion-resistant alloy (Haynes Stellite 19), by charging a 5.0 g sample to
 35 the 9.53 mm inside diameter cylinder which is

with a gas inlet tube at the bottom and vapor outlet port on the top. The vapor space/cube volume ratio was 1.8. Anhydrous ammonia (approximately 1.5 lbs) was introduced into the vessel through the gas inlet tube over a 15 minute period. The inlet and outlet tubes were then capped and the polymer cubes were allowed to stand in contact with the dilute ammonia atmosphere for a 24 hour period at 22-25°C. The vessel outlet port was then fitted to an exhaust system while nitrogen was blown through the inlet tube to displace the NH₃ treatment vapor. As shown below, infrared analysis of the polymer end groups before and after ammonia vapor treatment show that the carbonyl fluoride groups were converted to amide groups.

<u>Number of End Groups/10⁶C</u>			
	<u>End Group Functionality</u>	<u>Before NH₃ Treatment</u>	<u>After NH₃ Treatment</u>
20	-COF	26	0
	-CO ₂ H	0	0
	-CO ₂ CH ₃	39	56
	-CONH ₂	0	36
	-CH ₂ OH	197	210

The polymer was tested for fluoride ion extractability both before and after NH₃ treatment. Results were as follows:

Extractable Fluoride Ion Content

	<u>Before NH₃ Treatment</u>	<u>After NH₃ Treatment</u>
30	22.8 ppm	1.0 ppm

Stabilization of the carbinol end groups to heat aging was demonstrated as follows: Samples of the polymers described above, before and after

END GROUPS NO/10⁶ CARBONS IN

RESIN BEFORE
NH₃ TREATMENT

RESIN AFTER
NH₃ TREATMENT

TIME-HOURS
AT 295°C

	-COF	-CO ₂ H	-CO ₂ CH ₃	-CONH ₂	-CH ₂ OH	-COF	-CO ₂ H	-CO ₂ CH ₃	-CONH ₂	-CH ₂ OH
0	26	0	39	0	197	0	0	56	36	210
1	18	9	45	0	152	3	0	47	30	214
2	19	8	61	0	160	0	0	45	30	211
4	35	9	49	0	122	0	0	42	38	193
6	67	-	56	0	38	0	0	41	28	198
8	68	-	-	0	0	0	0	32	28	168



European Patent
Office

EUROPEAN SEARCH REPORT

0178935

Application number

EP 85 30 7506

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	FR-A-2 096 180 (DUNLOP HOLDINGS) * Claims 1,4-6,8,15 *	1	C 08 F 8/30
A	US-A-3 299 019 (T.J. KEALY) * Claims 1,2 *	1	
D,A	US-A-3 642 742 (D.P. CARLSON) * Claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-11-1985	Examiner PERMENTIER W.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	